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Introductory Chapter: Prospects of Nanostructured Materials

Sadia Ameen

1. Introduction

In the past few decades, there has been a worldwide surge of research interests in the field of nanoscience and nanotechnology. It has been realized that it has an impeccable potential to revolutionize the modern technology in countless ways. The field of “nanoscience” has attracted much attention from scientists and engineers due to its interesting scientific aspects, and the materials thus formed have novel physicochemical properties. In the beginning, the “miniaturization” of new devices and systems being the central theme of modern technologies was considered, but these days the subject of “nanomaterials” indeed happens to be very demanding. It has overwhelming contribution in technological advancement which has already started to have a global commercial impact.

In scientific terms, nanomaterials are basically any substance having a size of the order of 10^{-9} m, i.e., a billionth of a meter, and they are generally considered as “nanomaterials” when their sizes are typically lesser than 100 nm. In other words, nano-sized materials are the “collection of distinguishable units,” each of which is made up of a limited number of atoms. These units have specific shape and crystallinity and have at least one of its dimensions of about a few nanometers. A few common examples of naturally occurring nanomaterials are particulate matter from volcanic eruptions, different types of bacteria, cosmic dust, protrusions on lotus leaf that limits its wettability, etc. Also there are numerous man-made nanomaterials which include but are not limited to fullerenes, graphene, single-/multi-walled carbon nanotubes (CNTs), silver nanoparticles, metal oxide nanorods, quantum dots, etc. These nanomaterials have fascinating properties and, hence, are technologically important. For instance, due to the appropriate magnitudes of tensile strength, stiffness, and conductivity, graphene or CNTs have potential applications in catalysis, sensors, and drug deliveries. Nano-sized silver has displayed its capability of oxygen inhibition which could be utilized to pacify the burn injuries of living organisms. On the other hand, quantum dots of semiconducting materials are best suited in display and device technologies related to LED, memory storage, and solar cells [1–3]. In this manner, a variety of nanomaterials are potentially applicable in every sphere of modern technology which includes automotive, aerospace, cutting and device manufacturing industries, printing and color imaging, armor, computer chips, and biomedical and pharmaceutical fields as well.

The fact that attributes a special character to nanomaterials and variation in their overall behavior is their significantly small size. This generates “statistical size effect” that plays a vital role in altering most of the physical and chemical properties of these materials. Due to the reduction of the size to very small dimensions, typically 1–100 nm, more and more atoms are exposed to the surroundings and result into a vast increment of surface area to volume ratio for that

material. This material property is particularly responsible for assigning high specific surface area to the material, which remarkably improves many processes such as adsorption, catalysis, charge storage, and transfer on the surface of the material and hence opens avenues for its applications in sensors, supercapacitors, and batteries as well. Another feature associated to the reduction of particle size down to nano-regime is “quantum confinement effect.” The valence and free electrons of atoms in these nano-sized assemblies undergo considerable variations in their energy states as compared to their features in the macroscopic state. This affects the electronic band structure of the material in such a way that the separations between the continuous energy bands or the individual electronic energy levels alter. Subsequently the occupation and transition of electrons in these levels also change substantially which results into variation in the electronic, magnetic, and optical properties of that material [4]. There are numerous such examples wherein physical/chemical properties have been remarkably improved or modified through controlling the sizes and shapes of nanostructures. These interesting variations highlight the need of nanomaterials in newer technologies, and hence the designing and development of nanomaterials with tailor-made properties fitting specific applications happens to be the current goal of researchers working in this field. Efforts are also being taken to synthesize nanomaterials in different shapes such as nanorods, nanoparticles, nanobelts, nanotubes, and nanoshells with variations in their compositions as well.

Efficient synthesis of nanomaterials has always been a worldwide challenge. Numerous methods have already been devised and are also evolving continuously to fulfill this need. Methods such as auto-combustion, hydrothermal, coprecipitation, and sol-gel can be categorized as chemical methods to synthesize nanomaterials [5–8], whereas the methods such as solid-state route and high-energy mechanical milling can be termed as the physical methods. Also there are some more sophisticated techniques such as thermal evaporation, chemical vapor deposition, sputtering, pulsed laser ablation, pyrolysis, spin coating, etc. for the synthesis of high-quality thin films having nanocrystalline properties [9–11]. Every technique has its own merits and peculiarities for the synthesized nanomaterial. The solid-state methods are simple to yield the final product but may require high temperatures for the formation of desired compound. On the other hand, the deposition techniques are far more sophisticated than the other methods and hence become expensive; however, the synthesis can be controlled multi-parametrically which yield nanocrystalline thin films of superior quality. Using these techniques, variation in most of the properties such as morphology, composition, grain size, shape, thickness, crystal structure, and even non-equilibrium phases of synthesized materials could be achieved. With the advent of highly sophisticated analytical equipment such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), it is possible to observe and study these nano-sized materials from the point of view of future technological applications.

In the context of synthesizing nanomaterials, recently Ameen et al. discovered a fast and highly effective growth method for thin film of nanocrystalline tungsten oxide (WO_3) through one-step hot filament chemical vapor deposition (HFCVD) method at low temperature. The grown monoclinic WO_3 crystal structure exhibited the morphology of cauliflower-like nanostructure (WCNs). The grown WO_3 thin film was applied for the detection of hydrogen (H_2) gas at 100 ppm [11]. From the H_2 sensing behavior of WCN thin film, the appreciable sensitivity of the WCN thin film was obtained only after $\sim 200^\circ\text{C}$ and reached a

high magnitude of $\sim 87\%$ at optimum operating temperature of $\sim 250^\circ\text{C}$, as shown in **Figure 1**.

In year 2019, another work by Ameen and co-workers was reported on the synthesis of hexagonal zinc oxide (ZnO) nanopyramids (NPys) for the application of electrochemical sensor [12]. The synthesized hexagonal pyramid shape structures possessed the average size of $\sim 2\text{--}3\ \mu\text{m}$ with the base length of $\sim 2\ \mu\text{m}$ and a top length of $\sim 600\ \text{nm}$. From **Figure 2**, it is seen that the agglomeration of several hexagonal disks formed pyramid-like structures.

Nonenzymatic glucose biosensor was developed by utilizing the electrochemically grown nanocages-augmented polyaniline nanowires (NCA-PANI NWs) on silicon (Si) substrate [13]. Figure exhibits that the grown NCA-PANI NWs are distributed uniformly on the entire surface of silicon (Si) substrate, confirming the growth of highly dense NCA-PANI NW structures (**Figure 3**).

Kim et al. designed field effect transistor using iron-nickel co-doped ZnO nanoparticles, $\text{Zn}_{0.97}\text{Fe}_{0.01}\text{Ni}_{0.02}\text{O}$ NPs, for the electrochemical detection of hexahydropyridine chemical, as shown in **Figure 4** [14]. $\text{Zn}_{0.97}\text{Fe}_{0.01}\text{Ni}_{0.02}\text{O}$ NP-modified FET sensor showed the high sensitivity of $\sim 62.28\ \mu\text{A}\ \mu\text{M}^{-1}\ \text{cm}^{-2}$ and a good detection limit of $\sim 79\ \mu\text{M}$ with correlation coefficient (R) of ~ 0.96405 and a short response time (10 s) towards hexahydropyridine chemical.

Figure 5 shows the synthesized ZnO nanoflowers (NFs) for the photocatalytic degradation of bromophenol (Bph) dye. ZnO NFs as catalysts displayed a rapid degradation of Bph-dye with the degradation rate of $\sim 96\%$ within 120 min under the UV light irradiation [15].

Jang and co-workers synthesized porous cobalt oxide (Co_3O_4) nanocubes (NCs), as shown in **Figure 6**, and investigated the capacitive properties of porous Co_3O_4

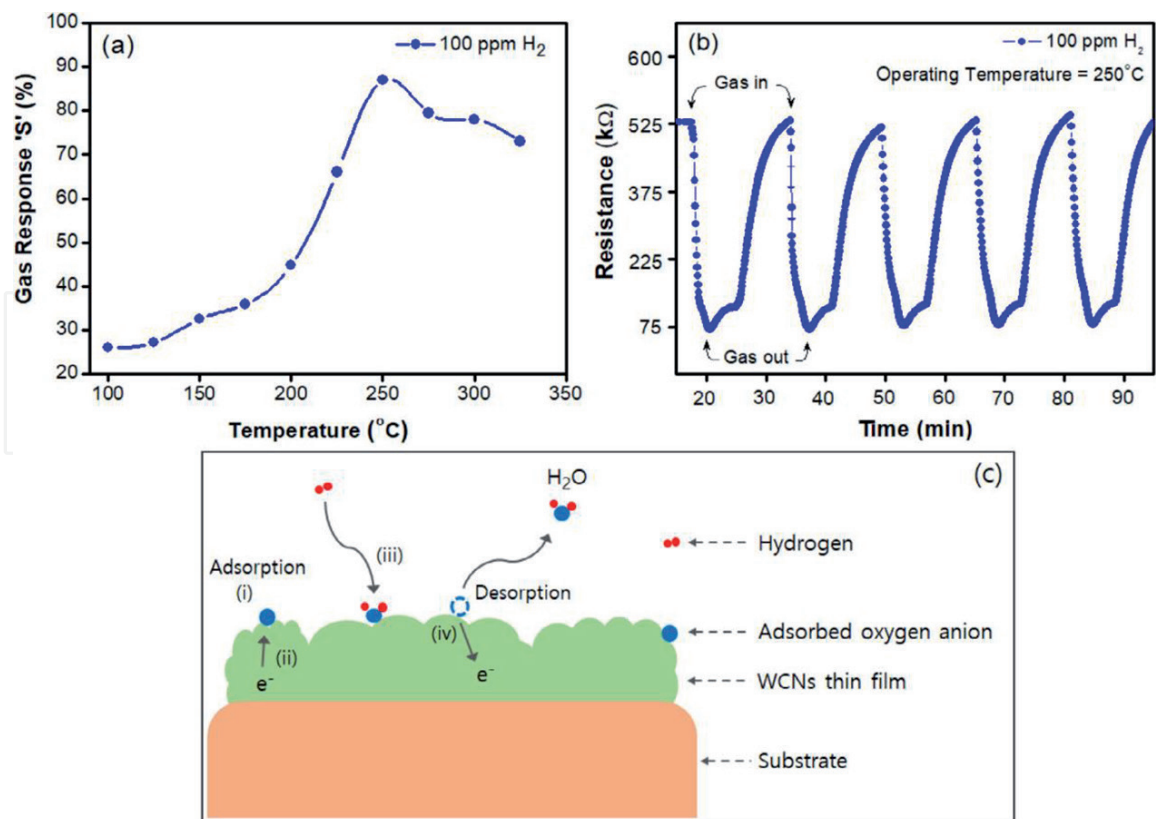


Figure 1.

(a) Gas sensing response of grown WO_3 thin film to H_2 gas at various temperatures, (b) response recovery profile with dynamic repeatability at $\sim 250^\circ\text{C}$ for 100 ppm H_2 , and (c) illustration of H_2 sensing mechanism on grown WO_3 thin film. Reproduced from reference [11].

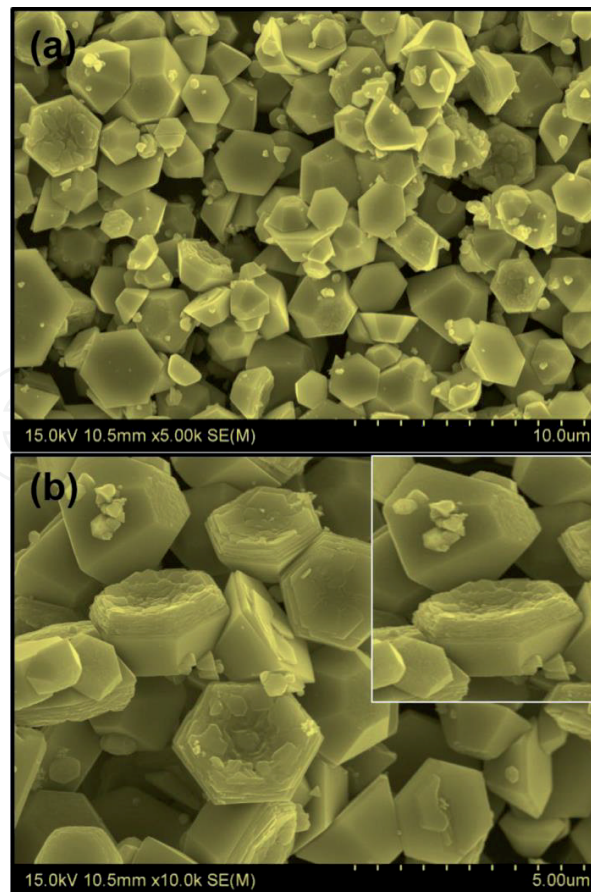


Figure 2. Low (a) and high (b) magnification FESEM images of hexagonal ZnO NPs. Reproduced from ref. [12].

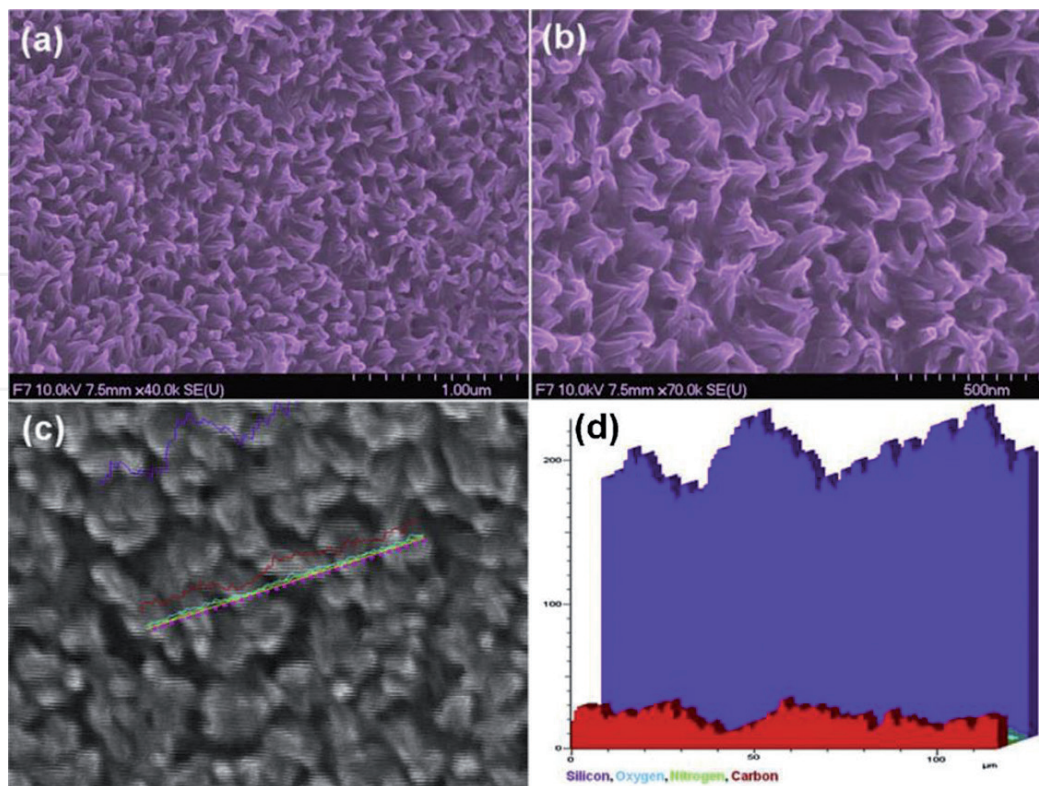


Figure 3. Low (a) and high (b) magnification FESEM images, element line scanning mapping (c), and its corresponding profile (d) of PANI NW electrode. Reproduced from ref. [13].

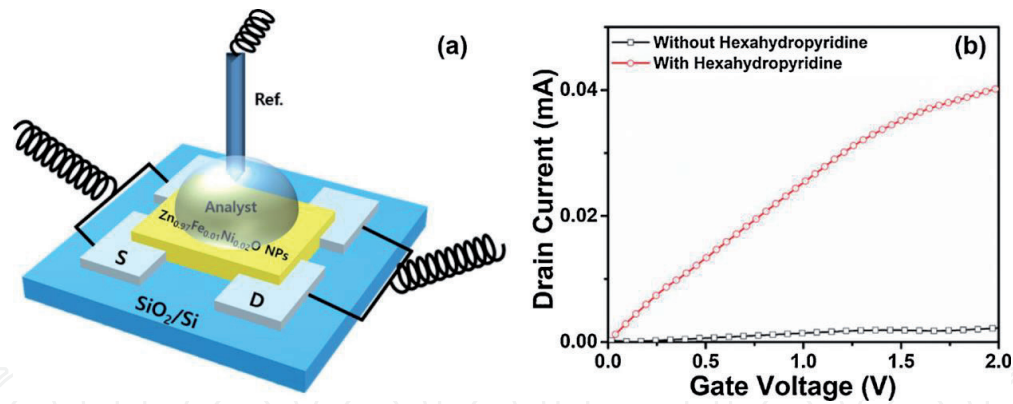


Figure 4. (a) A diagram represented the fabricated FET sensor with $Zn_{0.97}Fe_{0.01}Ni_{0.02}O$ NPs and (b) I_d-V_g response of FET sensor without and with hexahydropyridine (100 nM) in 0.01 M PBS. Reproduced from ref. [14].

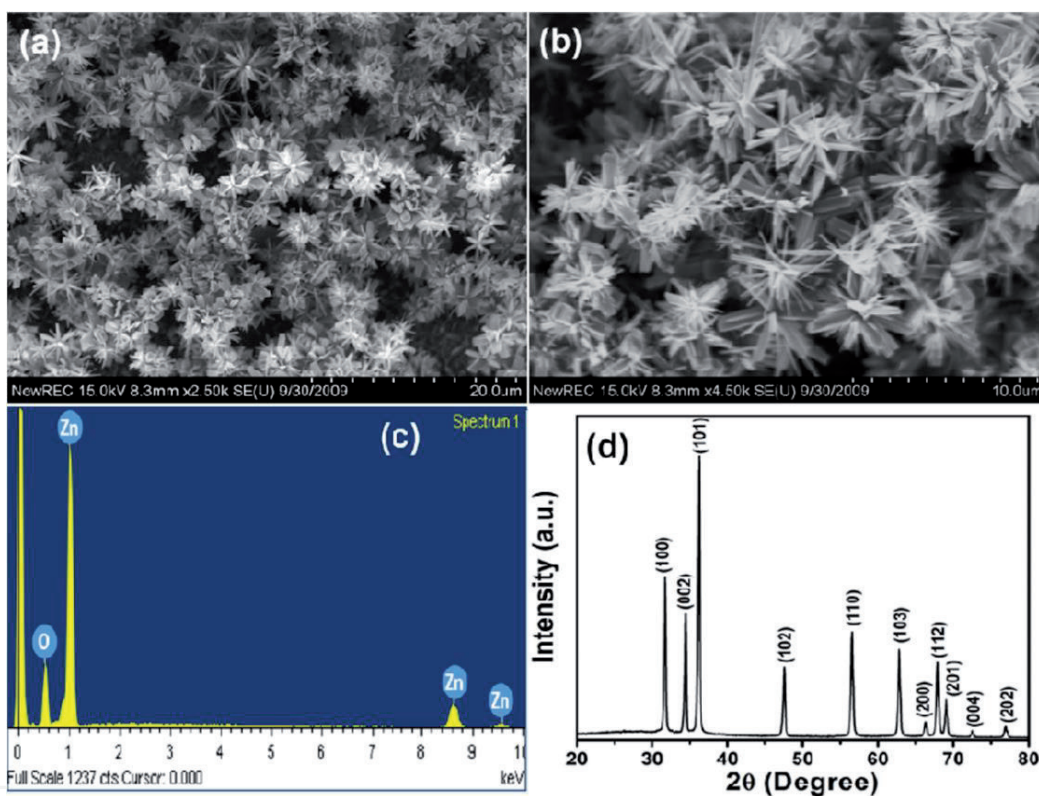


Figure 5. (a) Low and (b) high magnification FESEM images, (c) EDX spectrum, and (d) XRD analysis of ZnO NFs. Reproduced from ref. [15].

NCs electrode by cyclic voltammetry (CV) in 6 M KOH electrolyte. High specific capacitance of ~ 430.6 F/g at a scan rate of ~ 10 mV s⁻¹ was observed. The capacity retention of up to $\sim 85\%$ after 1000 cycles was shown by the fabricated porous Co₃O₄ NCs electrode. The porous Co₃O₄ NCs showed excellent structural stability through cycling with promising capacity retention which suggested a good quality of porous Co₃O₄ NCs as electrochemical supercapacitor electrode [16].

This prologue provides a glimpse of nanomaterials and the way their properties change and also gives an idea about their potent applicability which can shift the entire technological paradigm. This book has been designed to induce scientific interest in the minds of young researchers and engineers to undertake research in this field and work across the ever-expanding boundaries of nanoscience and nanotechnology.

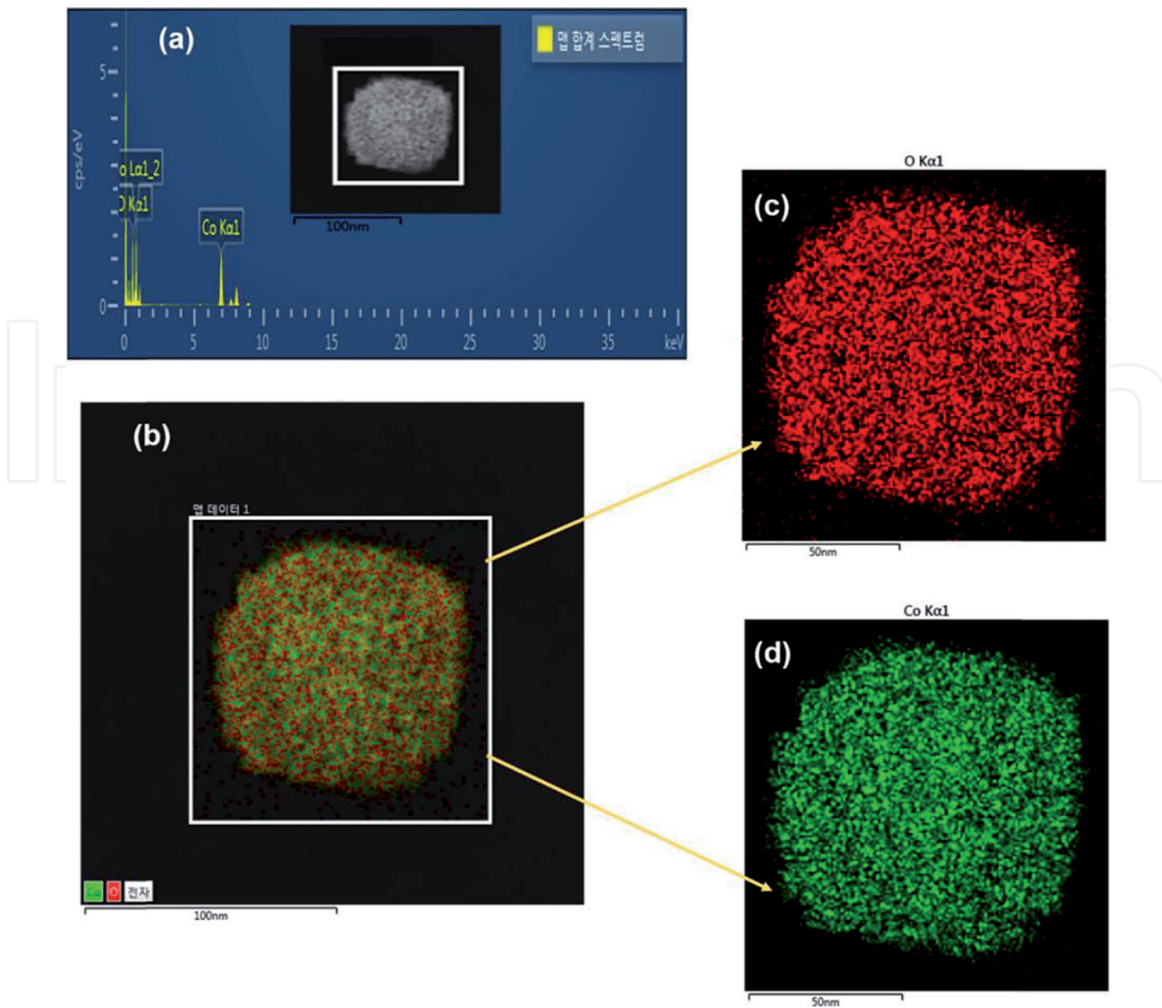


Figure 6. The representation of (a) TEM-EDX including profile and (b–d) elemental mapping images of porous Co_3O_4 NCs. Reproduced from ref. [16].

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